

PATENT SPECIFICATION

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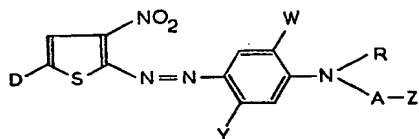


(54) DISPERSE AZO DYESTUFFS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to disperse monoazo dyestuffs which are valuable for colouring synthetic textile materials.

According to the invention there are provided the disperse monoazo dyestuffs, free from sulphonic and carboxylic acid groups, which are of the formula:—



wherein D is lower alkyl sulphonyl, lower alkyl carbonyl, sulphonoyl or optionally substituted benzoyl; R is lower alkyl, phenyl lower alkyl, cyano lower alkyl or a group —A—Z; A is a lower alkylene radical; W is hydrogen, chlorine, bromine, lower alkyl or lower alkoxy; Y is hydrogen, chlorine, bromine, lower alkyl, lower alkoxy or acylamino; and Z is a group of the formula —COOA'(X₁)_n, —O.CO.A'(X₂)_n or —OCOOB wherein A' is a saturated di- or tri-valent aliphatic hydrocarbon radical of from 1 to 4 carbon atoms or a di- or tri-valent benzene nucleus, n is 1 or 2, X₁ is cyano, hydroxy, acyloxy, lower alkoxy, carbo lower alkoxy, acyl, chlorine, bromine or phenyl, X₂ is cyano, hydroxy, acyloxy, lower alkoxy, acyl, chlorine, bromine or phenyl and B is an optionally substituted lower alkyl or phenyl radical.

Throughout this Specification the terms "lower alkyl", "lower alkoxy" and "lower alkylene" are used to denote alkyl, alkoxy and

alkylene radicals respectively containing from 1 to 4 carbon atoms.

As examples of the lower alkyl sulphonyl, lower alkyl carbonyl and substituted benzoyl radicals represented by D there may be mentioned methylsulphonyl, ethylsulphonyl, acetyl, propionyl, *p*-nitrobenzoyl, *o*-chlorobenzoyl and *m*-methoxybenzoyl.

As examples of the lower alkylene radicals represented by A there may be mentioned methylene, trimethylene, propylene, tetramethylene, α : β -dimethylethylene and preferably ethylene.

As examples of the lower alkyl and lower alkoxy radicals represented by W and Y there may be mentioned methyl, ethyl, methoxy, and ethoxy. The acylamino radicals represented by Y are preferably lower alkylsulphonylamino groups or acylamino groups of the formula —NHCOT wherein T is hydrogen or lower alkyl, and as examples of such radicals there may be mentioned formylamino, acetylamino and methanesulphonylamino.

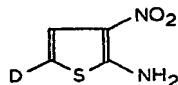
As examples of lower alkyl radicals represented by R there may be mentioned methyl, ethyl, *n*-propyl and *n*-butyl; and as examples of the phenyl lower alkyl radicals represented by R there may be mentioned benzyl and β -phenylethyl.

As examples of the radicals represented by A' there may be mentioned ethylene, trimethylene and 1:3- or 1:4-phenylene. It is preferred that n is 1 so that A' represents a divalent radical, in particular a divalent aliphatic hydrocarbon radical of from 1 to 4 carbon atoms.

As examples of the radicals represented by X₁ there may be mentioned carbo lower alkoxy such as carbomethoxy and carboethoxy and of the radicals represented by X₁ and X₂ independently there may be mentioned lower alkoxy such as methoxy and ethoxy, acyl in particular lower alkyl carbonyl such as acetyl and propionyl and also benzoyl, and acyloxy in particular groups of the formula O.COT wherein T is lower alkyl such as acetyloxy

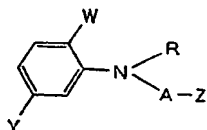
and propionyloxy. As examples of the optionally substituted lower alkyl and phenyl radicals represented by B there may be mentioned methyl, ethyl, *n*-propyl, benzyl, β -phenylethyl and phenyl. It is preferred that R is lower alkyl and X_1 or X_2 is cyano or lower alkoxy.

According to a further feature of the invention there is provided a process for the manufacture of the disperse monoazo dyestuffs of the invention which comprises diazotising an amine of the formula:—



Formula I

wherein D has the meaning stated, and coupling the resulting diazo compound with a coupling component of the formula:—



Formula II

wherein A, R, W, Y and Z have the meanings stated, the amine and coupling component being free from sulphonic acid and carboxylic acid groups.

The process of the invention can be conveniently carried out by adding sodium nitrite to a solution or dispersion of the amine in a strong inorganic acid or an aqueous solution thereof, or by stirring the amine with nitrosylsulphuric acid, and adding the resulting solution or dispersion of the diazo component to a solution of the coupling component in water containing an inorganic acid and/or a water-miscible organic liquid, if necessary adjusting the pH of the mixture to facilitate the coupling reaction, and finally isolating the resulting dyestuff by conventional methods.

The amines of Formula I can themselves be obtained by known methods, and as specific examples of such amines there may be mentioned 5-(acetyl-, propionyl- or *n*-butyryl-)-3-nitro-2-aminothiophene, 5-benzoyl-3-nitro-2-aminothiophene wherein the benzoyl radical can be substituted by nitro, chlorine or methoxy, and 5-(methylsulphonyl-, ethylsulphonyl-, *n*-propylsulphonyl-, or *n*-butylsulphonyl-)-3-nitro-2-aminothiophene.

As specific examples of the coupling components of Formula II there may be men-

tioned, for example, N-ethyl-N-(β -cyanomethoxycarbonylethyl)aniline, 2-methoxy-5-chloro-N-benzyl-N-(β -acetoxymethoxycarbonylethyl)aniline, N:N-di-(β -methoxycarbonyloxyethyl)-*m*-toluidine and 3-acetylamino-N-(β -phenoxy-carbonyloxyethyl)aniline.

The azo dyestuffs of the invention are valuable for colouring synthetic textile materials in particular secondary cellulose acetate and cellulose triacetate textile materials, polyamide textile materials such as polyhexamethylene adipamide textile materials, and, above all, aromatic polyester textile materials such as polyethylene terephthalate textile materials. Such materials can be in the form of filaments, fibres or woven or knitted materials.

The said azo dyestuffs can be applied to the synthetic textile materials by the methods which are conventionally employed in applying disperse dyestuffs to such textile materials. Thus the dyestuffs in the form of aqueous dispersions can be applied by dyeing, padding or printing processes using the conditions and other additives which are conventionally used in carrying out such processes. Alternatively, the said dyestuffs can be applied to synthetic textile materials by solvent methods of dyeing, for example by applying a solution or dispersion of the dyestuff in perchloroethylene optionally contain a minor amount of water to the textile material preferably at elevated temperature.

When applied to synthetic textile materials the azo dyestuffs of the invention give red to green colourations which have excellent fastness to light and to wet and to dry heat treatments. The said dyestuffs also have excellent build-up properties on synthetic textile materials, particularly aromatic polyester textile materials, thus enabling heavy depths of shade to be readily obtained.

The dyestuffs of the present invention are superior to the dyestuffs which are specifically described in Patent No. 774,611 in respect of their dyeing proportions on aromatic polyester textile materials and/or in respect of the heat fastness and/or light fastness of the resulting dyeings.

The invention is illustrated but not limited by the following Examples in which the parts and percentages are by weight.

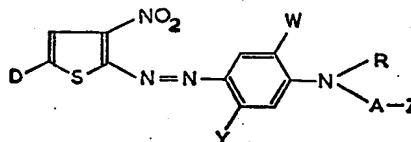
Example 1.

10 Parts of a sulphuric acid solution containing 1.35 parts of nitrosylsulphuric acid are added to a mixture of 8.6 parts of acetic acid and 1.4 parts of propionic acid at a temperature below 20° C. The solution is cooled to 10° C., 1.86 parts of 2-amino-3-

- nitro - 5 - acetylthiophene are added, and the mixture is stirred for 1 hour at 10° C. Urea is then added to destroy any residual nitrous acid, and the mixture is then added to a solution of 2.32 parts of N - ethyl - N - (β-cyanomethoxycarbonyl)ethyl)aniline in a mixture of 10 parts of acetone, 6 parts of a 2N aqueous solution of hydrochloric acid and 100 parts of ice. Sodium acetate is added to raise the pH of the mixture to 4, and the dyestuff which is formed is filtered off, washed with water and dried.

- When dispersed in aqueous medium the dyestuff dyes aromatic polyester textile materials in blue shades of excellent fastness properties.

- The following Table gives further Examples of the dyestuffs of the formula:—



the symbols of which have the values given in the respective columns of the Table. The last column of the Table gives the shades obtained when the dyestuffs are applied to an aromatic polyester textile material.

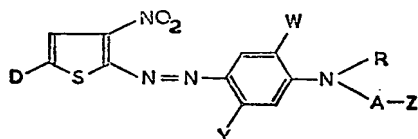
The dyestuffs of these Examples were obtained by methods similar to those described in Example 1 but starting from the appropriate amine and coupling agent.

Ex.	D	W	Y	R	—A—Z	Shade
2	acetyl	hydrogen	hydrogen	benzyl	β-(β'-methoxyethoxycarbonyl)-n-propyl	Blue
3	acetyl	hydrogen	acetyl-amino	β-(β'-methoxyethoxycarbonyl)ethyl	β-(β'-methoxyethoxycarbonyl)ethyl	Blue
4	acetyl	hydrogen	acetyl-amino	ethyl	β-(β'-methoxyethoxycarbonyl)ethyl	Blue
5	acetyl	hydrogen	hydrogen	ethyl	β-(p-chlorobenzoyloxy)-ethyl	Blue
6	acetyl	hydrogen	hydrogen	β-(p-methoxybenzoyloxy)-ethyl	β-(p-methoxybenzoyloxy)-ethyl	Blue
7	acetyl	hydrogen	hydrogen	ethyl	β-(β'-acetyloxyethoxycarbonyl)-ethyl	Blue
8	acetyl	hydrogen	hydrogen	β-cyano-ethyl	β-(β'-hydroxyethoxycarbonyl)-ethyl	Navy-blue
9	acetyl	hydrogen	hydrogen	ethyl	β-(β'-methoxycarbonylethoxycarbonyl)ethyl	Navy-blue
10	acetyl	hydrogen	methyl	ethyl	β-(β'-acetyloxyethoxycarbonyl)-ethyl	Greenish-blue

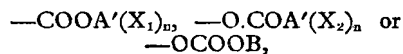
Ex.	D	W	Y	R	—A—Z	Shade
11	acetyl	hydrogen	methyl	ethyl	β -(β' -bromoethoxycarbonyl)-ethyl	Greenish-blue
12	acetyl	hydrogen	methyl	ethyl	β -(β' : γ' -dibromopropoxy carbonyl)-ethyl	Greenish-blue
13	methane-sulphonyl	methoxy	methoxy	ethyl	β -(β' -methoxyethoxycarbonyl)-ethyl	Greenish-blue
14	benzoyl	methoxy	methoxy	ethyl	β -(β' -methoxyethoxycarbonyl)-ethyl	Greenish-blue
15	<i>m</i> -methoxybenzoyl	methoxy	methoxy	ethyl	β -(β' -methoxyethoxycarbonyl)-ethyl	Greenish-blue
16	<i>m</i> -nitrobenzoyl	hydrogen	acetyl-amino	β -cyanoethyl	β -(β' -hydroxyethoxycarbonyl)-ethyl	Bluish-green
17	methane-sulphonyl	methyl	hydrogen	β -cyanoethyl	β -(β' -hydroxyethoxycarbonyl)-ethyl	Blue

WHAT WE CLAIM IS:—

1. The disperse monoazo dyestuffs, free from sulphonic and carboxylic acid groups, which are of the formula:—



- wherein D is lower alkyl sulphonyl, lower alkyl carbonyl, sulphonoyl or optionally substituted benzoyl; R is lower alkyl, phenyl lower alkyl, cyano lower alkyl or a group —A—Z; A is a lower alkylene radical; W is hydrogen, chlorine, bromine, lower alkyl or lower alkoxy; Y is hydrogen, chlorine, bromine, lower alkyl, lower alkoxy or acyl-amino; and Z is a group of the formula



wherein A' is a saturated di- or tri-valent aliphatic hydrocarbon radical of from 1 to 4

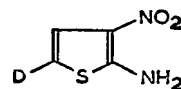
carbon atoms or a di- or tri-valent benzene nucleus, *n* is 1 or 2, X₁ is cyano, hydroxy, acyloxy, lower alkoxy, carbo lower alkoxy, acyl, chlorine, bromine or phenyl, X₂ is cyano, hydroxy, acyloxy, lower alkoxy, acyl, chlorine, bromine or phenyl and B is an optionally substituted lower alkyl or phenyl radical.

2. Dyestuffs as claimed in Claim 1 wherein *n* is 1 and A' is a saturated divalent aliphatic hydrocarbon radical of from 1 to 4 carbon atoms.

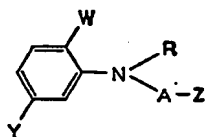
3. Dyestuffs as claimed in Claims 1 or 2 wherein R is lower alkyl and X₁ or X₂ is cyano or lower alkoxy.

4. Dyestuffs as claimed in any one of Claims 1 to 3 substantially as described herein and shown with reference to any one of the Examples.

5. Process for the manufacture of the dyestuffs as claimed in Claim 1 which comprises diazotising an amine of the formula:—



and coupling the resulting diazo compound with a coupling component of the formula:—



5 wherein A, D, W, Y and Z have the meanings stated in Claim 1, the amine and coupling component being free from carboxylic acid and sulphonic acid groups.

6. Process for the manufacture of the dye-stuffs as claimed in any one of Claims 1 to 4 substantially as described herein and shown with reference to any one of the Examples. 10

7. Process for colouring synthetic textile materials which comprises applying to the textile material a dyestuff as claimed in any one of Claims 1 to 4. 15

8. Process as claimed in Claim 7 wherein the synthetic textile material is an aromatic polyester textile material.

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